506. *Furans. Part II.*[1] *Friedel–Crafts Acylation of Furan, 2-Methylfuran, and 3-Methylfuran.*

By P. A. Finan and G. A. Fothergill.

Furan, 2-methylfuran, and 3-methylfuran with isovaleric anhydride under Friedel–Crafts conditions give the α-isovalerylfurans. The last of these (I; R = H, R′ = Me) was identical with elsholtzia ketone. 2-Acetyl-3-methylfuran (III) and 2-acetyl-4-methylfuran (V; R = Me) were prepared by unambiguous routes; the product obtained by acetylation of 3-methylfuran under Friedel–Crafts conditions was identical with the ketone (III), and contained no trace of the isomer (V; R = Me).

Elsholtzia ketone, found in the essential oils of *Elsholtzia cristata* Willd.,[2] *Perilla frutescens* Brit.,[3] and in *Elsholtzia oldhami* Hemsl.,[4] has structure (I; R = H, R′ = Me), on the basis of degradative[5] and synthetic work.[6] The tedious nature of the latter prompted us to attempt a synthesis by a Friedel–Crafts reaction on 3-methylfuran, an approach which had been successful for the synthesis[1] of the corresponding dehydro-compound, naginata ketone.

Treatment of furan with isovaleryl chloride in the presence of boron trifluoride in ether gave 2-isovalerylfuran (I; R = R′ = H) in 10% yield. When isovaleric anhydride was used the yield of ketone was increased to 55% (all yields are based on the anhydride). Similarly 2-methylfuran and isovaleryl chloride gave 2-isovaleryl-5-methylfuran (I; R = Me, R′ = H) in only 15% yield whereas use of isovaleric anhydride gave a 30% yield of ketone. 3-Methylfuran and isovaleryl chloride failed to give a ketonic product but use of isovaleric anhydride gave 2-isovaleryl-3-methylfuran (I; R = H, R′ = Me) in 30% yield. This product appeared to be homogeneous, had physical constants in agreement with those reported for elsholtzia ketone, and was indistinguishable from the natural product when chromatographed on thin layers of Kieselgel G. The infrared spectrum of the synthetic ketone was identical with that of elsholtzia ketone. The synthetic material gave a pair of isomeric 2,4-dinitrophenylhydrazones, m. p.s 126° and 189°, respectively, whose light absorption properties were identical with those reported for a corresponding pair (m. p.s 127—128° and 189—190°) prepared by Naves and Ochsner[4b] from the natural

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[1] Part I, *J.*, 1962, 2262.

[2] Asahina and Murayama, *Arch. Pharm.*, 1914, **252**, 435.

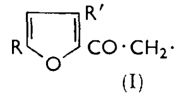
[3] Fujita and Ueda, *Nippon Kagaku Zasshi*, 1958, **79**, 1070.

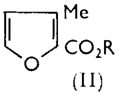
[4] (*a*) Fujita, *Nippon Kagaku Zasshi*, 1936, **57**, 574; 1958, **79**, 1067; (*b*) Naves and Ochsner, *Helv. Chim. Acta*, 1960, 406.

[5] Asahina, Murayama, Shibata, Kariyone, Kuwada, and Asano, *Acta Phytochim. Japan*, 1924, **2**, 1.

[6] Reichstein, Zschokke, and Georg, *Helv. Chim. Acta*, 1931, **14**, 1277.

product. The synthetic ketone gave a semicarbazone identical (m. p. and mixed m. p.) with a specimen prepared from the naturally occurring ketone.


(I)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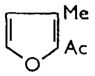
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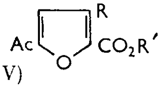
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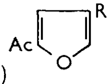
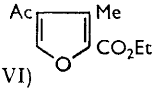

(V)


(VI)

This synthesis and the previous synthesis[1] of naginata ketone appear to involve electrophilic attack exclusively at the 2-position of 3-methylfuran. The preparation[6] of 3-methylfurfuraldehyde by the Gattermann reaction on 3-methylfuran, and the production[7] of 3-methyl-2-nitrofuran from 3-methylfuran by nitric acid–acetic anhydride, appear to be other examples of this specificity in the orientation of the incoming group. We now furnish proof that acetylation of 3-methylfuran with acetic anhydride in the presence of boron trifluoride in ether gave only the 2-acetyl isomer. We have prepared 2-acetyl-3- (III) and -4-methylfuran (V; R = Me) by unambiguous routes and have shown that the acetylation product of 3-methylfuran was identical with (III) and contained no trace of the isomer (V; R = Me).

2-Acetyl-3-methylfuran (III) was prepared in good yield by treatment of 3-methylfuroic acid (II; R = H) with ethereal methyl-lithium.[8]

As a preliminary to the preparation of 2-acetyl-4-methylfuran (V; R = Me) from ethyl 5-acetyl-3-methylfuroate (IV; R = Me, R′ = Et), the acetylation of ethyl furoate under Friedel–Crafts conditions was studied. This work is tabulated on p. 2726. Conditions were found in which treatment of ethyl furoate with acetic anhydride and stannic chloride gave ethyl 5-acetylfuroate (IV; R = H, R′ = Et) in 46% yield. The latter on saponification gave 5-acetylfuroic acid (IV; R = R′ = H), m. p. 198°. Gilman and Calloway[9] have reported that this compound "did not melt up to 230° but decomposed gradually with blackening." Our crystalline compound gave a crystalline 2,4-dinitrophenylhydrazone and on decarboxylation gave 2-acetylfuran (V; R = H).

Treatment of ethyl 3-methylfuroate (II; R = Et) with acetic anhydride and stannic chloride similarly gave crystalline ethyl 5-acetyl-3-methylfuroate (IV; R = Me, R′ = Et), although in poor (4%) yield. The proton magnetic resonance spectrum * of the compound gave a signal at τ 2·94 corresponding[10] to a 3-hydrogen atom (deshielded by the adjacent acetyl group) of the furan nucleus, confirming structure (IV; R = Me, R′ = Et) and eliminating structure (VI) which would be expected to show a signal for a 2-hydrogen atom of the furan nucleus having τ 2·0. Saponification of the ester gave crystalline 5-acetyl-3-methylfuroic acid (IV; R = Me, R′ = H), which on treatment with copper bronze and quinoline gave 2-acetyl-4-methylfuran (V; R = Me).

3-Methylfuran was treated with acetic anhydride and boron trifluoride in ether at 0°. A ketone (A) was obtained in 27% yield which was identical (physical constants; infrared and ultraviolet spectra; 2,4-dinitrophenylhydrazone; m. p. and mixed m. p.) with that (III) prepared from 3-methylfuroic acid. Both (A) and (III) had R_F 0·7 when chromatographed on thin layers of Kieselgel G in benzene–ether (4 : 1) whereas 2-acetyl-4-methylfuran (V; R = Me) had R_F 0·8. There was no chromatographically detectable trace of the latter in material (A).

It is noteworthy that by contrast with the results reported above for 3-methylfuran,

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* The spectrum was measured in CCl_4 solution (10%) with an AEI model RS2 spectrometer operating at 60 Mc./sec.; we thank Dr. R. A. Y. Jones for assistance with the interpretation.

[7] Gilman and Burtner, *J. Amer. Chem. Soc.*, 1933, **55**, 2903; Witte and Lind, U.S.P. 2,502,114/1950.

[8] Tegner, *Acta Chem. Scand.*, 1952, **6**, 782.

[9] Gilman and Calloway, *J. Amer. Chem. Soc.*, 1933, **55**, 4197.

[10] Leane and Richards, *Trans. Faraday Soc.*, 1959, **55**, 518.

treatment[11] of 3-methylthiophen with acetic anhydride and phosphoric acid gave a mixture of 2-acetyl-3- and 2-acetyl-4-methylthiophen in the ratio of ~4 : 1. Similarly, 3-methylthiophen and benzoyl chloride in the presence of aluminium chloride[12] gave a mixture of 2-benzoyl-3- and 2-benzoyl-4-methylthiophen.

EXPERIMENTAL

The alumina used was kept under ethyl acetate for 24 hr., washed with water, then with methanol, and dried at 200° for 4 hr. Ether extracts were dried over anhydrous sodium sulphate. Liquid products were distilled under nitrogen. The light petroleum used had b. p. 40—60°. M. p.s are uncorrected. Yields in acylations are based on the acyl reactant and are quoted to the nearest 5%.

Isovaleric Anhydride.—Isovaleric acid, on treatment with benzoyl chloride according to Brown's procedure,[13] gave isovaleryl chloride, b. p. 114° (lit., 114·5°). A mixture of isovaleryl chloride and isovaleric acid in benzene was treated with pyridine according to the procedure of Allen *et al.*[14] Isovaleric anhydride was obtained with b. p. 128—130°/20 mm. (lit., 103°/15 mm.).

2-*Isovalerylfuran* (I; R = R′ = H).—(a) *By using isovaleryl chloride.* Boron trifluoride in ether (45% w/w; 0·5 ml.) was added to furan (2·1 g., 0·03 mole) and isovaleryl chloride (3·6 g., 0·03 mole) at 0°. The mixture was shaken and then left at room temperature for 1 hr. Water was added and the dark mixture was extracted with ether. The extract was washed with water and aqueous sodium hydrogen carbonate, dried, and concentrated to a dark oil. This was chromatographed on alumina (light petroleum as eluant), giving a yellow oil which was distilled, to give 2-*isovalerylfuran* (0·5 g., 10%), b. p. 91—92°/20 mm., n_D^{25} 1·4885 (Found: C, 71·3; H, 7·7. $C_9H_{12}O_2$ requires C, 71·1; H, 7·9%), $\lambda_{max.}$ (in hexane) 263 and 272 mμ (ε 16,400 and 14,400, respectively), $\nu_{max.}$ 1670 (C=O) and 1565 cm.$^{-1}$ (furan).

The ketone, on treatment with 2,4-dinitrophenylhydrazine in ethanol containing sulphuric acid, gave a 2,4-*dinitrophenylhydrazone*, red plates (from ethyl acetate–methanol), m. p. 128° (Found: C, 53·6; H, 4·7; N, 16·7. $C_{15}H_{16}N_4O_5$ requires C, 54·3; H, 4·8; N, 16·9%), $\lambda_{max.}$ (in $CHCl_3$) 392 mμ (ε 26,100).

Treatment of the ketone with buffered semicarbazide in aqueous ethanol gave a *semicarbazone*, prisms (from ethanol), m. p. 170° (Found: C, 57·7; H, 7·1; N, 19·9. $C_{10}H_{15}N_3O_2$ requires C, 57·4; H, 7·2; N, 20·1%), $\lambda_{max.}$ (in EtOH) 289 mμ (ε 21,000).

(b) *By using isovaleric anhydride.* Boron trifluoride in ether (45% w/w; 0·5 ml.) was added to furan (2·2 g., 0·03 mole) and isovaleric anhydride (3·7 g., 0·02 mole) at 0°. The mixture was shaken and then left aside for 1 hr. Working-up as before gave 2-isovalerylfuran (1·7 g., 55%), b. p. 88°/20 mm., n_D^{25} 1·4889 (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 128°; semicarbazone, m. p. and mixed m. p. 170°).

2-*Isovaleryl*-5-*methylfuran* (I; R = Me, R′ = H).—(*a*) Boron trifluoride in ether (45% w/w; 0·5 ml.) was added to 2-methylfuran (2·6 g., 0·03 mole) and isovaleric anhydride (3·7 g., 0·02 mole) at 0°. After 1 hr. the mixture was worked up in the usual way. 2-*Isovaleryl*-5-*methylfuran* (0·9 g., 30%) was obtained as a pale yellow oil, b. p. 104°/25 mm., n_D^{25} 1·4936 (Found: C, 72·15; H, 8·1. $C_{10}H_{14}O_2$ requires C, 72·4; H, 8·4%), $\lambda_{max.}$ (in hexane) 273 and 282·5 mμ (ε 17,000 and 13,100, respectively), $\nu_{max.}$ 1670 (C=O), 1595, and 1520 cm.$^{-1}$ (furan).

The ketone, on treatment with 2,4-dinitrophenylhydrazine in ethanol containing sulphuric acid, gave a mixture of 2,4-dinitrophenylhydrazones which on fractional crystallisation from ethyl acetate–methanol gave *derivative* (1), orange needles, m. p. 142° (Found: C, 55·3; H, 5·0; N, 16·35. $C_{16}H_{18}N_4O_5$ requires C, 55·5; H, 5·2; N, 16·2%), $\lambda_{max.}$ (in $CHCl_3$) 394 mμ (ε 27,300), and derivative (2), brown needles, m. p. 173° (Found: C, 55·5; H, 5·0; N, 16·0%), $\lambda_{max.}$ (in $CHCl_3$) 403 mμ (ε 26,800).

The ketone afforded a semicarbazone, needles (from ethanol), m. p. 162° (Found: C, 58·5; H, 7·6; N, 18·6. $C_{11}H_{17}N_3O_2$ requires C, 59·2; H, 7·6; N, 18·8%), $\lambda_{max.}$ (in EtOH) 302 mμ (ε 18,800).

(*b*) Boron trifluoride in ether (45% w/w; 0·5 ml.) was added to 2-methylfuran (2·5 g.,

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[11] Hartough and Kosak, *J. Amer. Chem. Soc.*, 1947, **69**, 3093; Lamy, Lavit, and Buu-Hoï, *J.*, 1958, 4202.

[12] Steinkopf and Jacob, *Annalen*, 1935, **515**, 273.

[13] Brown, *J. Amer. Chem. Soc.*, 1938, **60**, 1325.

[14] Allen, Kibler, McLachlin, and Wilson, *Org. Synth.*, 1946, **26**, 1.

0·03 mole) and isovaleryl chloride (3·6 g., 0·03 mole) at 0°. The mixture was left aside for 1 hr. and was then worked up in the usual way. 2-Isovaleryl-5-methylfuran (0·7 g., 15%) was obtained as a yellow oil, b. p. 106°/25 mm., n_D^{25} 1·4958 (2,4-dinitrophenylhydrazones, m. p.s and mixed m. p.s 142° and 173°; semicarbazone, m. p. and mixed m. p. 162°).

2-Isovaleryl-3-methylfuran (I; R = H, R′ = Me).—Boron trifluoride in ether (45% w/w; 0·5 ml.) was added to 3-methylfuran (2·6 g., 0·03 mole) and isovaleric anhydride (3·7 g., 0·02 mole) at 0°. The mixture was kept at 0° for 1 hr. and was then worked up in the usual way. 2-Isovaleryl-3-methylfuran, elsholtzia ketone (0·9 g., 30%), was obtained as a pale yellow oil, b. p. 90°/20 mm., n_D^{25} 1·4842, $\lambda_{max.}$ (in hexane) 266 and 272 mμ (ε 11,900 and 9500, respectively) [lit.,[4b] b. p. 59·5—60°/2·2 mm., n_D^{20} 1·4868 $\lambda_{max.}$ (in iso-octane) 264 and 273 mμ (ε 16,000 and 12,600, respectively)] (Found: C, 72·35; H, 8·15. Calc. for $C_{10}H_{14}O_2$: C, 72·4; H, 8·4%). The infrared spectrum was identical with that of the naturally occurring ketone. Treatment of the ketone with 2,4-dinitrophenylhydrazine in ethanol containing sulphuric acid gave a mixture of 2,4-dinitrophenylhydrazones which on fractional crystallisation from ethyl acetate–methanol gave derivative (1), orange needles, m. p. 126° (Found: C, 54·9; H, 4·9; N, 16·0. Calc. for $C_{16}H_{18}N_4O_5$: C, 55·5; H, 5·2; N, 16·2%), $\lambda_{max.}$ (in $CHCl_3$) 384 mμ (ε 25,000), and derivative (2), red needles, m. p. 189° (Found: C, 54·6; H, 5·3%), $\lambda_{max.}$ (in $CHCl_3$) 400 mμ (ε 25,400), in agreement with Naves and Ochsner.[4b] Treatment of the ketone with buffered semicarbazide in aqueous ethanol gave a semicarbazone, m. p. 171°, undepressed on admixture with a specimen (supplied by Dr. Naves) prepared from the natural product.

2-Acetyl-3-methylfuran (III).—(*a*) *From 3-methylfuroic acid.* 0·75M-Ethereal methyllithium [8] (260 ml.) was added to 3-methylfuroic acid (10 g., 0·08 mole) in ether (200 ml.) under nitrogen. After the initial vigorous reaction, the mixture was heated under reflux for 1 hr., then cooled and treated with water, and the layers were separated. The ether layer, when worked up in the usual way, gave *2-acetyl-3-methylfuran* (5·7 g., 81% based on unrecovered acid), b. p. 60°/10 mm., n_D^{25} 1·4986 (Found: C, 68·3; H, 6·8. $C_7H_8O_2$ requires C, 67·7; H, 6·45%), $\lambda_{max.}$ (in hexane) 264 mμ (ε 11,400), $\nu_{max.}$ 1670 (C=O) and 1585 cm.$^{-1}$ (furan). It gave a *2,4-dinitrophenylhydrazone*, deep red needles (from ethanol), m. p. 180° (Found: C, 51·15; H. 4·1; N, 18·4. $C_{13}H_{12}N_4O_5$ requires C, 51·3; H, 3·95; N, 18·4%), $\lambda_{max.}$ (in $CHCl_3$) 400 mμ (ε 25,600).

3-Methylfuroic acid (3·0 g.) was recovered from the aqueous layer.

(*b*) *By Friedel–Crafts reaction.* Boron trifluoride in ether (45% w/w; 0·5 ml.) was added dropwise to 3-methylfuran (2·7 g., 0·03 mole) and acetic anhydride (5 g., 0·05 mole) at 0°. The mixture was kept at 0° for 1 hr. Working-up in the usual way gave 2-acetyl-3-methylfuran (1·1 g., 20%), b. p. 70—72°/20 mm., n_D^{25} 1·4960. The infrared spectrum was identical with that of the material prepared as in (*a*). The material had the same mobility on thin layer chromatograms as that prepared as in (*a*).

Acetylation of Ethyl Furoate.—Various conditions (see Table) were used in order to find a method for the efficient acetylation of ethyl furoate.

Et furoate (g.)	Ac_2O (g.)	$SnCl_4$ (g.)	Solvent	Reaction time (hr.)	Ester recovered (%)	Yield * of keto-ester (%)
4·2	3·1	15·7	Benzene	24	70	—
4·2	3·1	15·7	,, †	24	33	30
21·0	15·3	78·3	,, †	24	38	39
4·2	3·1	23·5	,, †	24	39	42 ‡
14·0	10·2	52·2	,, †	30	52	46 ‡
4·2	3·1	15·7	None	3	26	10 ‡
4·2	3·1	15·7	,,	24	—	—
4·2	3·1	15·7	,,	0·3	45	5 ‡
4·2	3·1	15·7	Toluene †	24	50	—

* The yield of keto-ester is based on unrecovered ethyl furoate. † Heated under reflux. ‡ The keto-ester was separated from unchanged ethyl furoate by chromatography on alumina; in other experiments the products were distilled.

Ethyl 5-Acetylfuroate (IV; R = H, R′ = Et).—A mixture of ethyl furoate (14 g., 0·1 mole) and acetic anhydride (10·2 g., 0·1 mole) in dry thiophen-free benzene (100 ml.) was added dropwise with stirring to stannic chloride (52·2 g., 0·2 mole) in dry thiophen-free benzene at 0°. The mixture was heated under reflux for 24 hr. After cooling, more acetic anhydride (5 g.) and stannic chloride (20 g.) were added and the mixture was heated under reflux for a further 6 hr., then cooled, poured into ice–water (600 ml.), and extracted with benzene. Working-up in the usual way gave a dark viscous oil, which was chromatographed on alumina. Elution with light petroleum gave unchanged ethyl furoate (4·1 g., 29%). Elution with benzene–light petroleum (1 : 1) gave ethyl 5-acetylfuroate (5·8 g., 45%), needles (from aqueous ethanol) m. p. 86° (lit.,[9] 86°).

5-*Acetylfuroic Acid* (IV; R = R′ = H).—Ethyl 5-acetylfuroate (5·8 g.) and potassium hydroxide (6 g.) in 50% aqueous ethanol (100 ml.) were heated under reflux for 6 hr. The mixture was cooled, acidified with dilute hydrochloric acid, and extracted with ethyl acetate. Working-up in the usual way gave a pale brown solid which was sublimed, giving 5-*acetylfuroic acid* (3·8 g., 77%), cream-coloured needles, m. p. 198° (Found: C, 54·5; H, 4·15. $C_7H_6O_4$ requires C, 54·5; H, 3·95%), $\nu_{max.}$ (in Nujol) 2800—2500 br (carboxylic acid dimer), 1670 (C=O), and 1555 cm.$^{-1}$ (furan) (lit.,[9] m. p. >230°). The acid gave a 2,4-*dinitrophenylhydrazone*, red needles (from ethanol), m. p. 252° (Found: C, 46·7; H, 3·7. $C_{13}H_{10}N_4O_7$ requires C, 46·6; H, 3·3%), $\lambda_{max.}$ (in $CHCl_3$) 389 mμ (ε 26,700).

A mixture of 5-acetylfuroic acid (0·77 g.), copper bronze (0·07 g.), and quinoline (1 ml.) was heated (metal-bath). Decarboxylation proceeded smoothly at 220°. The mixture was cooled and extracted with ether. Working-up in the usual way gave 2-acetylfuran, which was immediately converted into the 2,4-dinitrophenylhydrazone (0·82 g., 57%), m. p. 221° (lit.,[15] 223°).

Ethyl 5-*Acetyl*-3-*methylfuroate* (IV; R = Me, R′ = Et).—Ethyl 3-methylfuroate (22·8 g., 0·15 mole) and acetic anhydride (15·3 g., 0·15 mole) in dry thiophen-free benzene (150 ml.) were added slowly with stirring to stannic chloride (78·3 g., 0·3 mole) in benzene at 0°. The mixture was heated under reflux for 24 hr. More acetic anhydride (5 g.) and stannic chloride (20 g.) were added and the mixture was heated for a further 6 hr. After cooling, the mixture was worked up as usual. Ethyl 3-methylfuroate (2·2 g., 10%) was recovered unchanged. *Ethyl* 5-*acetyl*-3-*methylfuroate* (1·2 g., 4%) was obtained as pale yellow needles (from light petroleum), m. p. 96° (Found: C, 61·0; H, 6·15. $C_{10}H_{12}O_4$ requires C, 61·3; H, 6·15%), $\lambda_{max.}$ 278 and 289 mμ (ε 18,300 and 15,000, respectively), $\nu_{max.}$ 1710 (C=O of ester), 1680 (C=O of conjugated ketone), and 1600 cm.$^{-1}$ (furan), that gave 2,4-*dinitrophenylhydrazone*, red needles (from ethanol), m. p. 201° (Found: C, 50·6; H, 4·4. $C_{16}H_{16}N_4O_7$ requires C, 50·9; H, 4·5%), $\lambda_{max.}$ (in $CHCl_3$) 391 mμ (ε 29,500).

5-*Acetyl*-3-*methylfuroic Acid* (IV; R = Me, R′ = H).—Ethyl 5-acetyl-3-methylfuroate (0·8 g.) and potassium hydroxide (1 g.) in 50% aqueous ethanol (50 ml.) were heated under reflux for 6 hr. The mixture was cooled, acidified with dilute hydrochloric acid, and extracted with ether. Working-up in the usual way gave 5-*acetyl*-3-*methylfuroic acid* (0·44 g., 64%), off-white needles (from ethyl acetate), m. p. 202° (Found: C, 56·95; H, 4·9. $C_8H_8O_4$ requires C, 57·1; H, 4·75%) $\nu_{max.}$ (in Nujol) 2800—2150br (carboxylic acid dimer), 1670 (C=O), 1585 and 1520 cm.$^{-1}$ (furan).

2-*Acetyl*-4-*methylfuran* (V; R = Me).—5-Acetyl-3-methylfuroic acid (0·41 g.), copper bronze (0·04 g.), and quinoline (0·5 ml.) were heated (metal-bath) under reflux. Decarboxylation proceeded smoothly at 220—230°. When the required volume of carbon dioxide had been evolved the mixture was cooled and extracted with ether. The extract was washed with water, dried, and evaporated to a yellow oil (0·2 g.). In view of the small quantity of material, distillation was not attempted. The oil was chromatographed on a thick layer of Kieselgel G (prepared by Jones's method[16]) with benzene–ether (4 : 1) as developing solvent. The main component, visible under ultraviolet light, had R_F 0·8. The zone containing this material was scraped off the plate and extracted with ether. Removal of solvent *in vacuo* gave 2-*acetyl*-4-*methylfuran* (0·15 g., 55%), b. p. 188—192°/760 mm. (Found: C, 67·2; H, 6·8. $C_7H_8O_2$ requires C, 67·7; H, 6·45%), $\nu_{max.}$ 1680 (C=O of conjugated ketone), 1595 and 1495 cm.$^{-1}$ (furan). Its 2,4-*dinitrophenylhydrazone* formed red needles (from ethanol), m. p. 196° (Found: C, 51·05; H, 4·15. $C_{13}H_{12}N_4O_5$ requires C, 51·3; H, 3·95%), $\lambda_{max.}$ (in $CHCl_3$) 397 mμ (ε 26,200).

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[15] Chute, Orchard, and Wright, *J. Org. Chem.*, 1941, **6**, 157.

[16] Jones, D. N., personal communication.